Paul Scherrer Institute
CH-5232 Villigen PSI

Description

5

A process for the synthetic generation of methane

The invention relates to a process for the synthetic
generation of methane from a feed gas mixture comprising
10   carbon monoxide, hydrogen and water vapour and optionally
aromatic hydrocarbons.

It is the intention of the world-wide community to reduce the
production of gaseous climate relevant components, such as
15   chlorofluorocarbons (CFC) and carbon dioxide.For the carbon
dioxide the worldwide community committed itself to reduce the
production within the next decade in the range of about 10 to
15%, depending on the country and its commitment to the Kyoto
agreement.
20

So-called biofuels have the potential to influence the carbon
dioxide balance tremendously on a midterm and long-term basis
as being a relevant source for renewable primary products,
such as wood or related biomass. The estimated cost are
25   expected in the range of 300 Swiss Francs per ton of CO_2. These
costs are compared to other options taken in the
transportation sector quite inexpensive.

Beside natural gas (methane) and hydrogen the biofuels are
30   categorized as potential alternative. On a short-term fuels
like RME (bio diesel), ethyl alcohol and bio gas, are
available; in mid- to long-term, bio -fuels will be produced
according to the already theoretically well-known thermo-
chemical processes which take advantage of a catalyst in order
35   to transform a synthesis gas into the desired bio fuel, such
as methyl alcohol, synthetic gasoline or diesel, methane, or
hydrogen.

A most promising fuel is methane that is supplied actually as
fossil gas and which can be replaced under efficient use of
synergies between the required infrastructure for both the
5   fossil gas and the biogenic gas by the latter that can be
produced by fermentation as well as by thermo-chemical
processes.

Unfortunately, one of the most preferred renewable raw
10 material, wood, cannot be transformed into bio gas by
fermentation. Therefore, it is a crucial task to provide
efficient alternative processes for the synthetic generation
of methane from synthesis gas originating from wood
gasification processes.
15
A process known in the art uses wood in a gasification
reactor, such as FICFB (Fast Internally Circulation Fluidised
Bed), which requires subsequently non-negligible efforts for
the pretreatment of the raw synthesis gas in order to allow
20 both effective and efficient synthesis of methane. As far as
wood is considered as the renewable raw material, it has to be
pointed out that the raw synthesis gas originating from the
gasification step, is loaded with considerable amounts of
aromatic hydrocarbons and/or C_2 components which are known in
25 the prior art to have a negative impact in the subsequent
process chain. Therefore, the removal of these aromatic
hydrocarbons, such as benzene, toluene and naphthaline (BTN),
is acknowledged as being a required process requisite as well
as the removal of ammonia NH_3 and hydrogen sulfide H_2S.
30 Unfortunately, these additional process requisites tend to
increase the cost of the synthetic generation of methane from
woodand reduce the overall efficency.

For the reason given above, the crucial pre-requisite for an
35 efficient exploitation of wood for the synthetic generation of
methane is to find an optimized concert between the processes
of gasification, raw synthesis gas purification and methane

generation. Of central importance are the properties of the catalyst required for the generation of methane.

Accordingly, it is the aim of the invention to provide a
5 process which allows the synthetic generation of methane for a renewable raw material, explicitly including wood and related materials, in an economically and feasible manner.

This aim is achieved according to the invention by a process
10 for the synthetic generation of methane from a feed gas mixture, i.e. a feed gas mixture originating from a biomass gasification process, comprising carbon monoxide, hydrogen and water vapour and optionally C_2 components and/or aromatic hydrocarbons; said process comprising the steps of:
15   a) bringing the feed gas mixture in contact with a fluidized bed catalyst having catalyst particles which comprise as catalytic active component a metal and/or a metal compound or a mixture thereof;
   under the circumstances of:
20   b) an elevated temperature in the range of 250 to 500°C;
       c) a feed gas pressure in the range of 0.8 to 70 bar;
       d) a gas hourly space velocity of 1000 to 50000 h^{-1}; and
       e) a concentration of H_2/CO in the feed gas mixture in the range of 0.25 to 5.
25

The afore-mentioned process allows to catalytically convert hydrogen and carbon monoxide effectively in the fluidized bed. Using a fluidized bed catalytic reactor avoids a rapid deactivation of the catalyst material and therefore delivers a
30 high activity of the catalytic active components in the process.

Both thermo-chemical reactions, the endothermic reformation of higher hydrocarbons, i.e. aromatic hydrocarbons, and the

4

exothermic methane generation, proceed simulataneously within
the fluidized bed catalytic reactor, leading to an overall
enhanced thermal efficiency of the conversion process.

5 With respect to the initial and continuing catalytic activity,
excellent results have been achieved by using as catalytically
active component nickel and/or a nickel compound, preferably a
mixture of nickel and nickel monoxide, deposited on an ceramic
carrier, such as Al_2O_3, TiO_2, SiO_2 or Y_2O_3 or mixtures thereof.
10 Additionally, the content of the catalytically active
component may be in the range of 20 to 80 weight%, preferably
40 to 60 weight%, as compared to the weight of the catalyst
particles. A suitable catalyst may comprise nickel and nickel
oxide deposited on alumina (Al_2O_3) having a content of the
15 catalytically active component in the range of 50 weight% as
calculated as pure nickel.

In order to achieve both, a high mobility of the catalyst
particles in the fluidized bed, and a sufficient reactive
20 surface area, the size of the catalyst particles may be in the
range of 10 to 1000 μm, preferably in the range of 50 to 500
μm.

With respect to the energy balance of the exothermic
25 generation of methane an advantageous feed gas composition is
considered to have a positive impact thereupon when the feed
gas mixture comprises aromatic hydrocarbons, such as benzene,
toluene and naphthalene, in the range of less than 10 Vol%,
preferably less than 5 vol%. Explicitly, this gas composition
30 covers broadly a synthesis gas that originates from wood
gasification processes to which a major focus is laid upon due
to the environmental demands.

An optimal yield with respect to the generation of methane as well as to a complete conversion of the higher hydrocarbons may require that the gas hourly space velocity (GHSV) is in the range of 2000 to 10000 h^{-1}, the temperature is in the range of 340 to 400°C and the gas pressure is in the range of 0.8 to 10 bar. With respect to the above-mentioned nickel/nickel oxide catalyst, the temperature may preferably be at about 350°C, and the GHSV at about 4200 h^{-1} .

In order to offer conditions in the fluidized bed catalyst that support both the catalytic reactions of reforming higher hydrocarbons and formation of methane and the regeneration of the catalyst particles, a mean residence time of the feed gas mixture in the fluidized bed catalyst may range from 0.1 to 5 sec., preferably 0.2 to 1 sec.

Again with respect to the yield of methane and to the reformation of higher hydrocarbons the content of H_2/CO in the feed gas mixture is in the range of 0.8 to 3, for example in the range of 1.5 as combined with the afore-mentioned nickel/nickel oxide catalyst.

Exemplarily embodiments of the inventive process are described in detail below without the intention to limit the invention to these actually preferred examples.

Various measurements have been taken with a plant as shown schematically below in Figure 1. The measurement campaign can be divided in three different sections:

Phase 1: The feed gas mixture is pretreated with a wet scrubber unit and an activated carbon filter (charcoal absorber) as proposed so far in the prior art which teaches the process as being unactable

without prior gas cleaning and removal of aromatic
hydrocarbons;

Phase 2:   The feed gas mixture is now only pretreated with the
wet scrubber unit; charcoal absorber has been
bypassed being aware of a possible catalyst
deactivation reported so far in the prior art due to
carbon which is deposited on the catalytic surfaces
and by that blocks their reactivity (coking); and

Phase 3:   The feed gas mixture is taken as of the outlet of
the wood gasification plant without any pretreatment
as disclosed in the prior art.

Especially for the intention of maintaining the activity and
selectivity of the catalyst, unsaturated hydrocarbons (such as
C_2H_4, C_2H_2), light tar components (such as benzene, toluene,
naphthaline, phenylacethylene, styrole, indene) and ammonia
are known according to the prior art as being highly
disturbing these demands.

Figure 1 shows that the complete plant comprises an inlet at
1) for the feed gas mixture originating from a non-illustrated
wood gasification plant, followed by a wet scrubber unit at
2), an activated carbon filter at 3), a gas pump and the
methane generation unit COALA whereby the methane content is
observed at the outlet of COALA at 4). The methane generation
unit COALA comprises a desulphurisation unit in form of a ZnO
fixed bed reactor, an inlet for the supply of water vapour, a
fluidized bed catalyst, a filter and a heat exchanger as seen
in direction of the gas flow.

In phase 1, the washer unit for the removal of ammonia NH_3 and
the activated carbon filter for the removal of higher
hydrocarbons are installed upstream the methane generation
unit COALA.

The measurements have shown that all disturbing higher
hydrocarbons are already removed at 3) by both the wet
scrubber unit and the activated carbon filter which is the
desired effect of gas purification being declared as a pre-
requisite in the prior art for the efficient subsequent
methane generation. The plant was operated continuously at a
temperature of about 360°C, a water content of 0.25 as related
to the dry gas volume and a gas volume flow rate of 0.6 m^3/h.

During phase 2, the plant was operated without activated
carbon filter (bypassing line named Phase 2+3 in Fig. 1) and
the gas composition contained significant amounts of higher
hydrocarbons. Surprisingly, a reduction of the content of
higher hydrocarbons can be observed although the carbon filter
unit has been bypassed.

During phase 3, the plant was operated without any
pretreatment of the feed gas mixture according to the present
invention. As already before in phases 1 and 2, for the
fluidized bed catalyst 100 g catalyst particles having a size
of 200 µm and comprising an even content of nickel and nickel
oxide supported by alumina (Al_2O_3) whereby the content of the
catalytically active nickel components is 50 weight% as
calculated as pure nickel, was used. The gas composition for
the higher hydrocarbons can be compared to be in the same
range as during phase 2. At the entrance the average load of
benzene, toluene, naphthaline and C8 was in the range of 13.6
g/Nm^3 resp. 0.6 g/Nm^3 resp. 0.8 g/Nm^3 resp. 0.5 g/Nm^3. At the
outlet at 4) these higher hydrocarbons were reformed almost
completely without the occurrence of any catalyst deactivation
or loss in selectivity.

In evaluating the experimental data, the following definitions
have to be observed:

The steam/dry gas ratio

8

$$D_V = \frac{n_{H2O}}{n_{Gas\,tr.}} \quad [-]$$

is the molar ratio of water steam to all the other gas
components. The catalyst load is expressed as the ratio of the
number of moles of gas brought into contact with a given mass
of catalyst per hour.

$$KB = \frac{n_{Gas\,tr} + n_{H2O}}{M_{Kat}} \quad \left[\frac{mol}{kg \cdot h}\right]$$

originating from the generation of methane from synthesis gas,
such as pure H_2/CO gas. The „steam to carbon ratio"

$$S/C = \frac{n_{H2O}}{n_{Carbon}} \quad [-]$$

is the molar ratio of water steam to total amount of carbon in
the gas and is known from the steam reforming of methane. All
above mentioned key figures are used in a sense that clearly
determined distinct gas compositions were used. Therefore,
they are not sufficient in order to describe the process of
generating methane from a synthesis gas being achieved by a
biomass gasification process. Additionally, the H/C ratio in
both a dry product gas

$$H/C_{tr} = \frac{n_H}{n_C}$$

as well as in a humidified product gas

$$H/C_f = \frac{n_H + 2 \cdot n_{H2O}}{n_C}$$

is a suitable parameter to characterize the process properly.
A further meaningful parameter is the conversion rate of
carbon monoxide

$$U_{CO} = \frac{n_{COin} - n_{COout}}{n_{COin}} \quad [-] \, ,$$

the selectivity to methane

$$S_{CH4} = \frac{n_{CH4in} - n_{CH4out}}{(n_{COin} - n_{COout}) + x \cdot (n_{CxHyin} - n_{CxHyout})} \quad [-]$$

and the so called cold gas efficiency,

$$\eta_{KG} = \frac{Heatingvalue_{CH4out}}{Heatingvalue_{in}}$$

which describes the heating value of the methane at the outlet in relation to the overall heating value of the gas at the inlet.

Surprisingly, the catalyst does not show any effect of deactivation and/or loss in selectivity, even when continuously operating the plant over dozends of hours.